

# CHEMICAL EQUILIBRIUM -II |

## Structure

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## 6.1 INTRODUCTION

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Often, the chemist is in a situation, when he/she has to predict what will be the effect on the equilibrium of a chemical system when there is a change in the conditions. It has been seen that the equilibrium mixture responds to this change by shifting to a new equilibrium position, however, the equilibrium constant remains the same.

We have already dealt in the previous unit the reversible and irreversible reactions and Gibbs energy change in a chemical reaction. Also we have dealt in details the equilibrium constants-  $K_p$ ,  $K_c$  and  $K_x$  and the relation between them.

In this unit we are going to deal with the applications of equilibrium studies in both homogeneous and heterogeneous systems. Also we are going to discuss the Le Chatelier's Principle. Thereupon we are going to discuss the effect of change of concentration, or pressure, or temperature as well as the addition of inert gas or catalyst on the equilibrium.

## Expected Learning Outcomes

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| After studying this unit, you should be able to:

- ❖ describe the applications of equilibrium studies;

- ❖ state Le Chatelier's Principle;
- ❖ explain the effect of change in concentration, pressure, temperature to the chemical equilibrium;
- ❖ Predict the response of an equilibrium system to changes in conditions by applying Le Chatelier's principle;
- ❖ explain the effect of addition of inert gas to the chemical equilibrium; and
- ❖ describe the effect of a catalyst on a chemical equilibrium.

## 6.2 APPLICATIONS OF EQUILIBRIUM STUDIES

Let us start this unit by understanding how to apply the equilibrium studies in real life situations.

### 6.2.1 Determining Equilibrium Constants

At this stage, you must be aware that, whenever you have to determine the value of an equilibrium constant, you have to know the equilibrium concentrations of all of the concentrations that appear in the equilibrium constant expression. With the help of these values  $K_c$  is obtained.

Thus whenever you will be calculating equilibrium constants, at first you should make a table, which would show (i) initial conditions, (ii) changes that take place when a reaction occurs, (iii) final (equilibrium) conditions. Let us understand this with the help of the following examples.

#### Example 6.1: Determining an equilibrium constant value

Consider the colourless gas dinitrogen tetroxide,  $\text{N}_2\text{O}_4(g)$ . When heated it dissociates to form red-brown  $\text{NO}_2(g)$  according to the equation



a)



b)

**Fig. 6.1: a) The formation of brown  $\text{NO}_2$  in the boiling water increases.  
b) The ice cold container, which contains more molecules of colourless  $\text{N}_2\text{O}_4$ , so its colour is lighter.**

For example, let us take that 2.00 mol  $\text{N}_2\text{O}_4(g)$  is placed into an empty 5.00 L flask and heated to 407 K. Almost immediately a dark red-brown colour appears. So it indicates that the colourless gas  $\text{N}_2\text{O}_4$  has been transformed

into red-brown  $\text{NO}_2$  (Fig. 6.1a). By measuring the intensity of colour, it can be determined that the concentration of  $\text{NO}_2$  at equilibrium is 0.525 mol/L. To use this information to calculate the equilibrium constant, follow these steps:

- Firstly, you should write down the balanced equation for the reaction for which you are going to calculate the equilibrium constant of the reaction. From it derive the equilibrium constant expression. The balanced equation and equilibrium constant expressions are

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad \dots(6.1)$$

- Next you must enter the values of initial concentration, change in concentration, and equilibrium concentration for each substance included in the equilibrium constant expression in a proper table. Now, if you can check the data: we have the number of moles of  $\text{N}_2\text{O}_4(g)$  and the volume of the flask. Now let us calculate the initial concentration of  $\text{N}_2\text{O}_4(g)$  as (conc.  $\text{N}_2\text{O}_4$ ) = 2.00 mol/5.00 L = 0.400 mol/L. In the initial condition, as there was no  $\text{NO}_2$ , the initial concentration of  $\text{NO}_2$  is zero. After the reaction took place and equilibrium was reached, the equilibrium concentration of  $\text{NO}_2$  was measured as 0.525 mol/L. The reaction table looks like this:

|                                   | $\text{N}_2\text{O}_4(g)$ | $\rightleftharpoons$ | $2\text{NO}_2(g)$ |
|-----------------------------------|---------------------------|----------------------|-------------------|
| Initial concentration (mol/L)     | 0.400                     |                      | 0                 |
| Change as reaction occurs (mol/L) | ---                       |                      | ---               |
| Equilibrium concentration (mol/L) | ---                       |                      | 0.525             |

- Now, let us take the change in concentration of one substance to be  $x$ . Use the stoichiometric coefficients in the balanced equilibrium equation to calculate the other changes in terms of  $x$ . As the reaction proceeds from left to right, the concentrations of reactants decrease. So the change in concentration of a reactant should be negative and the change in concentration of a product should be positive. In this problem, you have been given both initial and equilibrium concentrations of  $\text{NO}_2$ . So let us take  $x$  to be the change in concentration of  $\text{NO}_2$  which is not known.

|                                   | $\text{N}_2\text{O}_4(g)$ | $\rightleftharpoons$ | $2\text{NO}_2(g)$ |
|-----------------------------------|---------------------------|----------------------|-------------------|
| Initial concentration (mol/L)     | 0.400                     |                      | 0                 |
| Change as reaction occurs (mol/L) | ---                       |                      | $x$               |
| Equilibrium concentration (mol/L) | ---                       |                      | 0.525             |

Next, we use the mole ratio from the balanced equation to find the change in concentration of  $\text{N}_2\text{O}_4$  in terms of  $x$ .

$$\begin{aligned} \Delta(\text{conc. } \text{N}_2\text{O}_4) &= \frac{x \text{ mol } \text{NO}_2 \text{ formed}}{\text{L}} \times \frac{1 \text{ mol } \text{N}_2\text{O}_4 \text{ formed}}{2 \text{ mol } \text{NO}_2 \text{ formed}} \\ &= \frac{1}{2} x \text{ mol } \text{N}_2\text{O}_4 \text{ reacted/L} \end{aligned}$$

The sign of the change in concentration of  $\text{N}_2\text{O}_4$  is negative, because the concentration of  $\text{N}_2\text{O}_4$  decreases. The table becomes

|                                   | $\text{N}_2\text{O}_4(g)$ | $\rightleftharpoons$ | $2\text{NO}_2(g)$ |
|-----------------------------------|---------------------------|----------------------|-------------------|
| Initial concentration (mol/L)     | 0.400                     |                      | 0                 |
| Change as reaction occurs (mol/L) | $-\frac{1}{2}x$           |                      | $x$               |
| Equilibrium concentration (mol/L) | -                         |                      | 0.525             |

4. Now, you take the values of initial concentrations and the changes in concentrations and calculate the equilibrium concentrations in terms of  $x$  and enter them in the table. The concentration of  $\text{N}_2\text{O}_4$  at equilibrium,  $[\text{N}_2\text{O}_4]$ , is thereby the sum of the initial 0.40 mol/L of  $\text{N}_2\text{O}_4$  and the change due to reaction  $-\frac{1}{2}x$  mol/L; that is,  $[\text{N}_2\text{O}_4]_{\text{eqm}} = (0.40 - \frac{1}{2}x)$  mol/L. In the same way, the equilibrium concentration of  $\text{NO}_2$  (which is already known to be 0.525 mol/L) is  $0 + x$ , and the table becomes

|                                   | $\text{N}_2\text{O}_4(g)$ | $\rightleftharpoons$ | $2\text{NO}_2(g)$ |
|-----------------------------------|---------------------------|----------------------|-------------------|
| Initial concentration (mol/L)     | 0.400                     |                      | 0                 |
| Change as reaction occurs (mol/L) | $-\frac{1}{2}x$           |                      | $x$               |
| Equilibrium concentration (mol/L) | $0.400 - \frac{1}{2}x$    |                      | $0.525 = 0 + x$   |

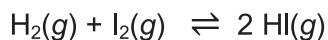
5. Use the simplest possible equation to solve for  $x$ . Then use  $x$  to calculate the unknown you were asked to find. (Usually the unknown is  $K_c$  or a concentration.) In this case, the simplest equation to solve for  $x$  is the last entry in the table,  $0.525 = 0 + x$ , and it is easy to see that  $x = 0.525$ . Calculate  $[\text{N}_2\text{O}_4] = (0.400 - \frac{1}{2}x)$  mol/L =  $(0.400 - \frac{1}{2} \times 0.525)$  mol/L = 0.138 mol/L. The problem stated that  $[\text{NO}_2] = 0.525$  mol/L, so  $K_c$  is given by

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.525 \text{ mol/L})^2}{(0.138 \text{ mol/L})} = 2.00 \text{ (at 407 K)}$$

6. In this case the equilibrium concentration of product is larger than the concentration of reactant. So you should have a value greater than 1.

### Example 6.2: Determining an equilibrium constant value

Consider the gas phase reaction



Let the above reactants of initial concentrations of each 0.0175 mol/L be heated to 425°C. What happens after some time? Well, concentrations of  $\text{H}_2$  and  $\text{I}_2$  decrease whereas the concentration of  $\text{HI}$  increases. At equilibrium  $[\text{HI}] = 0.0276$  mol/L. Use this experimental information to calculate the equilibrium constant.

**Answer:**  $K_c = 56$

### Solution

The above information is to be used and the six steps to be followed.

1. Write the balanced equation and equilibrium constant expression.



2. Next, enter the known information in a proper table.  
3. Represent changes in concentration in terms of  $x$ .

You should enter  $x$  in the third column, because both initial and equilibrium concentrations of HI are known. So, easily you can calculate  $x$ . Next, derive the rest of the concentration changes in terms of  $x$ . If the concentration of HI increases by a given quantity, the mole ratios say that the concentrations of  $\text{H}_2$  and  $\text{I}_2$  must decrease only half as much:

$$\frac{x \text{ mol HI produced}}{\text{L}} \times \frac{1 \text{ mol H}_2 \text{ consumed}}{2 \text{ mol H}_2 \text{ produced}}$$

$$= \frac{1}{2} x \text{ mol/L H}_2 \text{ consumed}$$

Because the coefficients of  $\text{H}_2$  and  $\text{I}_2$  are equal, each of their concentrations decreases by  $\frac{1}{2}x$  mol/L. The entries in the table for change in concentration of  $\text{H}_2$  and  $\text{I}_2$  are negative, because their concentrations decrease.

4. Calculate equilibrium concentrations and enter them in the table.

|                                      | $\text{H}_2(g)$         | $+ \text{I}_2(g)$       | $\rightleftharpoons 2 \text{HI}(g)$ |
|--------------------------------------|-------------------------|-------------------------|-------------------------------------|
| Initial concentration<br>(mol/L)     | 0.0175                  | 0.0175                  | 0                                   |
| Change as reaction<br>occurs (mol/L) | $-\frac{1}{2}x$         | $-\frac{1}{2}x$         | $x$                                 |
| Equilibrium<br>concentration (mol/L) | $0.0175 - \frac{1}{2}x$ | $0.0175 - \frac{1}{2}x$ | $0.0276 = 0 + x$                    |

5. Now let us solve equations to find the value of  $x$ . The last row and column in the table contains  $0.0276 = 0 + x$ , which gives  $x = 0.0276$ . Substitute this value into the other two equations in the last row of the table to get the equilibrium concentrations, and substitute them into the equilibrium constant expression:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.0276)^2}{\left(0.0175 - \left[\frac{1}{2} \times 0.0276\right]\right)\left(0.0175 - \left[\frac{1}{2} \times 0.0276\right]\right)}$$

$$= \frac{(0.0276)^2}{(0.0037)(0.0037)} \text{ (at } 424^\circ\text{C}) = 55.6$$

Is the answer correct? You see, here the equilibrium constant is greater than 1, so there should be more products than reactants when equilibrium is reached. The equilibrium concentration of the product (0.0276 mol/L) is larger than those of the reactants (0.0037 mol/L each).

Experimentally determined equilibrium constants for a few reactions are given in Table 6.1. These reactions occur to widely differing extents, as shown by the wide range of  $K_c$  values.

**Table 6.1: Selected Equilibrium Constants at 25°C**

| Reaction  | $K_c$                            | $K_p$                  |
|---|----------------------------------|------------------------|
| $\frac{1}{8} S_8(s) + O_2(g) \rightleftharpoons SO_2(g)$                              | $4.2 \times 10^{52}$             | $4.2 \times 10^{52}$   |
| $2 H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$                                       | $3.2 \times 10^{81}$             | $1.3 \times 10^{80}$   |
| $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  | $3.5 \times 10^8$                | $5.8 \times 10^5$      |
| $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$   | $4.5 \times 10^{-31}$            | $4.5 \times 10^{-31}$  |
|   | $1.7 \times 10^{-3}$ (at 2300 K) |                        |
| $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$   | $2.5 \times 10^1$                | $2.5 \times 10^1$      |
| $2NO_2(g) \rightleftharpoons N_2O_4(g)$   | $1.7 \times 10^2$                | 7.0                    |
| $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$                                | $2.0 \times 10^{-28}$            | $1.25 \times 10^{-25}$ |
| <i>Cis</i> -2-butene( $g$ ) $\rightleftharpoons$ <i>trans</i> -2-butene ( $g$ )       | 3.2                              | 3.2                    |
| <b>Weak acids and bases</b>   |                                  |                        |
| Formic acid<br>$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$       | $1.8 \times 10^{-4}$             | -----                  |
| Acetic acid<br>$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ | $1.8 \times 10^{-5}$             | -----                  |
| Carbonic acid<br>$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$  | $4.2 \times 10^{-7}$             | -----                  |
| Ammonia (weak base)<br>$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$  | $1.8 \times 10^{-5}$             | -----                  |
| <b>Very slightly soluble solids</b>   |                                  |                        |
| $CaCO_3(s) \rightleftharpoons Ca^+(aq) + CO_3^{2-}(aq)$                               | $3.8 \times 10^{-9}$             | -----                  |
| $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$                                      | $1.8 \times 10^{-10}$            | -----                  |
| $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$  | $1.5 \times 10^{-16}$            | -----                  |

## 6.2.2 The Significance of the Value of Equilibrium Constant

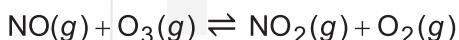
The value of the equilibrium constant gives us the information how far the reaction has proceeded when the equilibrium has been achieved. Also, it can be used to calculate how much product will be present at equilibrium. There are three important cases to consider.

### Case 1

The symbol  $\gg$  means "much greater than".

**$K_c \gg 1$ :** In this case, reaction is strongly product-favoured; you should understand that the concentrations of products are much greater than concentrations of reactants under equilibrium conditions.

Whenever it is a large value of  $K_c$ , most reactants have been converted to products when equilibrium has been achieved. That is, the products are strongly favoured over the reactants. An example is the reaction of  $\text{NO}(g)$  with  $\text{O}_3(g)$ , which is one way that ozone is destroyed in the stratosphere.



$$K_c = \frac{[\text{NO}_2][\text{O}_2]}{[\text{NO}][\text{O}_3]} = 6 \times 10^{34} \quad (\text{at } 25^\circ\text{C}) \quad \dots(6.3)$$

The reaction goes to completion only when equilibrium has been reached. If reaction is slow this could take a lot of time.

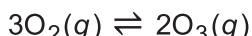
The very large value of  $K_c$  tells us that if 1 mole each of  $\text{NO}$  and  $\text{O}_3$  are mixed in a flask at  $25^\circ\text{C}$  and allowed to come to equilibrium,  $[\text{NO}_2][\text{O}_2] \gg [\text{NO}][\text{O}_3]$ . So, only  $\text{NO}_2$  and  $\text{O}_2$  will be found in the flask. For practical purposes, this reaction goes to completion, and it would not be necessary to use the equilibrium constant to calculate the quantities of products that would be obtained.

### Case 2

The symbol  $\ll$  means "much less than".

**$K_c \ll 1$ :** Reaction is strongly reactant-favoured; concentrations of reactants are greater than concentrations of products under equilibrium conditions.

On the other hand, an extremely small  $K_c$  means that when equilibrium has been achieved, very little of the reactants have been transformed into products. The reactants are favoured over the products at equilibrium. An example is



$$K_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3} = 6.25 \times 10^{-58} \quad (\text{at } 25^\circ\text{C})$$

So you can say that,  $[\text{O}_3]^2 \ll [\text{O}_2]^3$  and if  $\text{O}_2$  is placed in a flask at  $25^\circ\text{C}$ , very little  $\text{O}_3$  will be found when equilibrium is achieved. There will be no change in the concentration of  $\text{O}_2$ . We would write "N.R." and say that no reaction occurs.

### Case 3

**$K_c \approx 1$ : Equilibrium mixture contains significant concentrations of reactants and products; calculations are needed to determine equilibrium concentrations.**

Whenever  $K_c$  is neither extremely large nor extremely small, the equilibrium constant must be used to calculate how far a reaction proceeds toward products. In contrast with the reactions in Case 1 and Case 2, dissociation of dinitrogen tetroxide has neither a very large nor a very small equilibrium constant. At 391K the value is 1.00, which means that significant concentrations of both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are present at equilibrium.

$$K_c = 1.00 \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

So  $[\text{NO}_2]^2 = [\text{N}_2\text{O}_4]$  (at 391 K) ... (6.4)

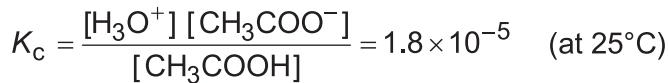
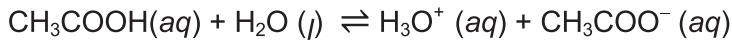
If the concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at equilibrium are both 1.0 mol/L, then the ratio of  $[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$  does equal the  $K_c$  value of 1.00 at 391 K. Can you say what would happen if the concentrations were much smaller? Would they still be equal? You can verify this by using Eq.6.4. Let us take the value of the equilibrium concentration of  $\text{NO}_2$  to be 0.01, then the concentration of  $\text{N}_2\text{O}_4$  must be  $(0.01)^2$ , which equals 0.0001. Thus, even though  $K_c = 1.00$ , the concentration of one substance can be much larger than the concentration of the other. This happens because there is a squared term in the numerator of the equilibrium constant expression and a term to a different power (the first power) in the denominator. So you see, whenever the total of the exponents in the numerator is not the same as the total in the denominator, it will not be possible for you to confirm which concentration will be more, that of the reactants or the products, unless and until you do a calculation.

On the other hand, if the total of the exponents is the same, then if  $K_c > 1$ , products predominate over reactants, and if  $K_c < 1$ , reactants predominate over products. Example,



At this stage, a question may arise in your mind, are reactant - favoured systems in which small quantities of products form are important? Well, in many cases they are. Examples include the acids and bases listed in Table 6.1.

For acetic acid, the acidic ingredient in vinegar, the reaction is



The value of  $K_c$  for acetic acid is small, and under equilibrium conditions the concentrations of the products (acetate ions and hydronium ions) are much

smaller than the concentration of the reactant (acetic acid molecules). So you see that acetic acid is a weak acid.

Now you see, the equilibrium reactions are similar and the equilibrium constant expressions all have the same form for formic acid, acetic acid, and carbonic acid:

$$K_c = \frac{[\text{H}_3\text{O}^+] [\text{anion}^-]}{[\text{acid}]}$$

where  $\text{anion}^-$  is  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ , or  $\text{HCO}_3^-$ , and acid is  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ , or  $\text{H}_2\text{CO}_3$ . From data in Table 6.1, we can say that formic acid is stronger (has a larger  $K_c$  value) than acetic acid and of the three acids carbonic acid is the weakest. So you see, since the pattern of the equilibrium constant is the same for these reactions, you can quantitatively compare the extent to which the reaction is product-favoured.

If the forward reaction has a large tendency to occur, then the reverse reaction has little tendency to occur. This means that the equilibrium constant for the reverse of a strongly product-favoured reaction will be extremely small. Table 6.1 shows that combustion of hydrogen to form water vapour has an enormous equilibrium constant ( $3.2 \times 10^{81}$ ). This reaction is strongly product-favoured. We say that it goes to completion.

The reverse reaction, decomposition of water to its elements, is strongly reactant-favoured, as indicated by the very small value of  $K_c$ .



$$K_c = \frac{[\text{H}_2]^2 [\text{O}_2]}{[\text{H}_2\text{O}]^2} = 3.1 \times 10^{-82} \text{ (at } 25^\circ\text{C})$$

### *SAQ 1*

Use equilibrium constants (Table 6.1) to predict which of the reactions given below will be product-favoured at  $25^\circ\text{C}$ . Place all of the reactions in order from most reactant-favoured to least reactant-favoured.

- $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$
- $\text{HCOOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCOO}^-(aq)$
- $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

### **6.2.3 Using Equilibrium Constants**

Because equilibrium constants have numeric values, you would be able to predict quantitatively the direction of a reaction.

#### **Predicting the Direction of a Reaction**

Let us start with a mixture of 50.00 mmol  $\text{NO}_2(g)$  and 100.00 mmol  $\text{N}_2\text{O}_4(g)$  at  $25^\circ\text{C}$  in a container with a volume of 10 L. Will you be able to say whether it is

in equilibrium? Otherwise, in which direction will it react to achieve equilibrium? In such cases you should use the reaction quotient,  $Q_c$ , which has the same mathematical form as the equilibrium constant expression but is a ratio of actual concentrations in the mixture, instead of equilibrium concentrations.

You know that,

- If  $Q_c$  is equal to  $K_c$  then the reaction is at equilibrium. The concentrations will not change.
- If  $Q_c$  is less than  $K_c$  then the concentrations of products are not as large as they would be at equilibrium. The forward reaction will occur and the products will form till equilibrium is reached.
- If  $Q_c$  is greater than  $K_c$ , then the product concentrations are bigger than they would be at equilibrium. The reverse reaction will proceed from right to left and reactants will form till equilibrium is reached.

For the reaction

$$2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \quad K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = 1.7 \times 10^2 \text{ (at } 25^\circ\text{C)}$$

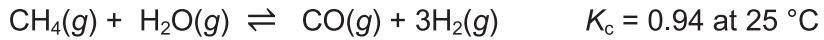
$$\begin{aligned} Q_c &= \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{(100.00 \times 10^{-3} \text{ mol}/10\text{L})}{(50.00 \times 10^{-3} \text{ mol}/10\text{L})^2} \\ &= \frac{1.0 \times 10^{-2}}{(5.0 \times 10^{-3})^2} = 4.0 \times 10^2 \end{aligned}$$

In the above example,  $Q_c$  is greater than  $K_c$ , so, in order to attain equilibrium, some  $\text{N}_2\text{O}_4$  will react to form  $\text{NO}_2$ . As the reverse reaction takes place,  $Q_c$  becomes smaller and eventually becomes equal to  $K_c$ .

### Example 6.3:

#### Predicting direction of reaction

Consider the equilibrium of the reaction used to generate hydrogen gas industrially.



If 1.0 mole  $\text{CH}_4$ , 1.0 mole  $\text{H}_2\text{O}$ , 2.0 mole  $\text{H}_2$ , and 0.50 mole  $\text{CO}$  are mixed in a 10.0 L container at  $25^\circ\text{C}$ , will the concentration of  $\text{H}_2\text{O}$  be greater or less than 0.10 mol/L when equilibrium is reached?

**Answer:** Less than 0.10 mol/L

#### Solution

Calculate the initial concentration of each gas and thus evaluate  $Q_c$ . Then compare  $Q_c$  with  $K_c$ .

$$[\text{CH}_4] = \frac{1.0 \text{ mol}}{10.0 \text{ L}} = 0.10 \text{ mol/L} \quad [\text{H}_2] = \frac{2.0 \text{ mol}}{10.0 \text{ L}} = 0.20 \text{ mol/L}$$

$$[\text{H}_2\text{O}] = \frac{1.0 \text{ mol}}{10.0 \text{ L}} = 0.10 \text{ mol/L} \quad [\text{CO}] = \frac{0.50 \text{ mol}}{10.0 \text{ L}} = 0.050 \text{ mol/L}$$

Because the units are defined by the equilibrium constant expression, leave them out.

$$Q_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = \frac{(0.050)(0.20)^3}{(0.10)(0.10)} = 0.040$$

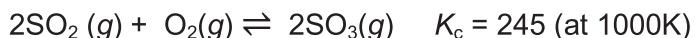
which is much smaller than 0.94, the value of  $K_c$ . Because  $Q_c < K_c$ , the forward reaction, i.e. a reaction of  $\text{CH}_4$  with  $\text{H}_2\text{O}$  to form  $\text{CO}$  and  $\text{H}_2$ , will occur until the equilibrium concentrations are reached. The initial concentration of  $\text{H}_2\text{O}$  was 0.10 mol/L; when  $\text{H}_2\text{O}$  reacts with  $\text{CH}_4$ , the  $\text{H}_2\text{O}$  concentration decreases.

Now we shall discuss how to draw qualitative conclusions without actual calculations. Because all concentrations are fractions, multiplying concentrations will give smaller fractions. The concentrations are of the order  $10^{-1}$ , but the numerator has concentration to the fourth power and the denominator to the second power overall. This means that  $Q_c$  would be much less than 1 and the reaction will occur in forward direction before equilibrium is reached. Therefore, the concentration of  $\text{H}_2\text{O}$  would decrease and become less than 0.10 mol/L.

So we can say if the value of  $Q_c$  is much smaller than the value of  $K_c$ , the reaction will move to the forward direction. Similarly, when the value of  $Q_c$  is much larger than that of  $K_c$ , the reaction will move in the reverse direction.

### *SAQ 2*

For the equilibrium



The equilibrium concentrations are  $[\text{SO}_2] = 0.102$ ,  $[\text{O}_2] = 0.0132$ , and  $[\text{SO}_3] = 0.184$ . Suppose that the concentration of  $\text{SO}_2$  is suddenly doubled. Calculate  $Q_c$  and use it to show that the forward reaction would take place to reach a new equilibrium.

## **6.3 LE CHATELIER'S PRINCIPLE**

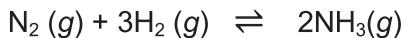
Whenever there is a slight disturbance in the system at equilibrium either by a change in the temperature or the concentration of reactants or products, the system will react in response to the change. In this section, we will discuss how changes in these factors influence the composition of the equilibrium mixture and the value of the equilibrium constant.

Whenever there is a change in the concentration or the partial pressures of any of the reactants or products, the composition of a system at equilibrium

changes. Henri Louis Le Chatelier (1850-1936) was the first one to describe qualitatively how these changes influence a chemical reaction at equilibrium.

Le Chatelier's principle can be written as: Any change to a chemical reaction at equilibrium causes the reaction to proceed in the direction that reduces the effect of the change.

Whenever there is a change in concentration, pressure, or temperature, the concerned reaction proceeds in the direction that reduces the impact of the change. Let us take the following example of the formation of ammonia:



Now, can you predict what would happen if you added hydrogen, to the equilibrium mixture of nitrogen, hydrogen, and ammonia? Le Chatelier's principle predicts that a reaction will occur to reduce the change. In this case concentration changed, because the concentration of hydrogen increased, so the system proceeds in that direction to decrease the concentration of hydrogen (and nitrogen) concentration by forming more ammonia. Whereas, if the hydrogen would be removed, the system would proceed in the direction where it forms more hydrogen (and nitrogen).

The Le Chatelier's principle is utilised by the chemists to improve the yield of reaction. Suppose there is a way of removing ammonia as soon as it forms, then the reaction will continue until either the nitrogen or the hydrogen is all used up. Now, how do you remove ammonia? It is seen that ammonia can easily be liquefied at modest pressure, whereas nitrogen and hydrogen cannot be. A reactor can be designed to operate at a moderate pressure and separate the liquid from the gases. Whenever the liquid ammonia is removed, the system thereby produces more. The process continues to produce ammonia until the nitrogen or hydrogen is consumed.

Efficient production of ammonia is an important issue because ammonia is an important industrial product, with uses ranging from fertilizer to rocket fuels.

Now we will discuss the effects of change of concentration, or pressure, or temperature, as well as the addition of inert gas or catalyst on the equilibrium.

### **6.3.1 Effect of Change of Concentration**

In order to understand the concepts in a better way, let us take the following examples.

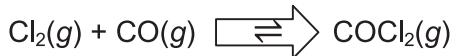
**Example 6.4:** You all must be knowing that the Bhopal plant made phosgene,  $\text{COCl}_2$ , on-site. The reaction of carbon monoxide and chlorine to form phosgene, like any equilibrium system, shows the effects of changes in concentration.



Can you say what will be the direction of reaction if carbon monoxide is added?

The first way we might look at the problem is to use Le Chatelier's principle and state that the reaction will proceed to consume some of the added carbon

monoxide. Because carbon monoxide is a reactant, the reaction will form some additional product in response to this change.



The symbol  $\rightleftharpoons$  is generally used to indicate that the reaction proceeds to the right, to use up added carbon monoxide, but the equilibrium constant does not change.

We can also arrive at a solution to the problem by seeing how an increase in the concentration of [CO] changes  $Q_c$ . Let us start with the equilibrium constant expression from the chemical equation.

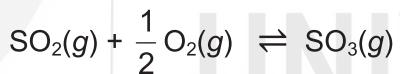
$$K_{\text{eq}} = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$$

$K_{\text{eq}}$  is calculated from the concentrations of all the species at equilibrium. If carbon monoxide is added to the equilibrium mixture, then  $Q_c$  is smaller than  $K_{\text{eq}}$  and the reaction proceeds towards the right, to form more phosgene and use up some of the added CO.

Now, with the help of Example 5, you will understand how a system responds when the equilibrium concentrations are disturbed.

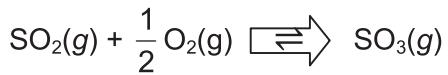
#### Example 6.5: How do you predict the direction of a reaction when the system is disturbed?

In which direction does the reaction proceed when sulphur dioxide is added to an equilibrium mixture of oxygen, sulphur dioxide, and sulphur trioxide?



**Note:** This you should solve with the help of Le Chatelier's principle.

**Solution:** If the concentration of  $\text{SO}_2$  increases, then the reaction will proceed in the direction that decrease the concentration of the added substance.  $\text{SO}_3$  will form as  $\text{SO}_2$  is consumed.



An alternative to applying Le Chatelier's principle involves comparing  $Q_c$  and  $K_{\text{eq}}$ . The equilibrium constant expression is

$$K_{\text{eq}} = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$$

If  $\text{SO}_2$  is added to the system,  $Q_c$  becomes smaller than  $K_c$  and the reaction proceeds to the right.

**Answer:** To the right, to produce more  $\text{SO}_3$ .

### 6.3.2 Effect of Change of Pressure

Changes in the partial pressures of gases have the same effects as change in concentration, because pressure is just another measure of concentration. So you can change partial pressures of the reacting species by adding (or removing) either the reactants or products. Also, it can be done by changing the volume of the reaction vessel. In the following example, you will see the effect of changing the volume of the container.

#### Example 6.6:

##### How the equilibrium system responds to change in volume?

Some  $\text{PCl}_5$  is placed in a 10.0 L reaction cylinder. The temperature is increased to 500 K, and the following reaction reaches equilibrium.



Now, let us investigate a situation where increase in the external pressure decreases the volume to 1.0 L. You must keep the temperature constant at 500 K.

#### Note

Le Chatelier's principle should be utilised. The system will proceed in that direction where the effect of the change is minimized.

#### Solution

As there is a reduction in the volume, the concentrations (partial pressures) of the species increase. Why is it so? It is because the same numbers of moles are now in a smaller volume. The system responds to reduce the effect of this change by decreasing the number of moles of gases. We look at the chemical equation and see that the reactant side of the equation has 1 mole gas ( $\text{PCl}_5$ ), but the product side has 2 moles of gases  $\text{PCl}_3$  and  $\text{Cl}_2$ .



1 mole gas on reactant side  $\rightleftharpoons$  2 moles of gas on product side.

In this case, if you Increase the external pressure, there will be a decrease in the volume of the system, so the reaction will proceed in the direction which will reduce the number of moles of gases. So here, if you decrease the volume, more reactants will be formed.

#### SAQ 3

Ammonia is formed by the reaction of nitrogen and hydrogen, all in the gas phase ( $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ ). After the system reaches equilibrium, the volume of the container is decreased. In which direction does the reaction proceed?

**Table 6.1: Relationship between Change in Number of Moles of Gases in a Reaction and Response of the System to Changes in Volume and Pressure**

| Example   | $\Delta n_g$ | Decrease in Volume (or increase in external pressure) favours formation of | Increase in Volume (or decrease in external pressure) favours formation of |
|---|--------------|--|--|
| $\text{CaCO}_3(\text{s}) + 3\text{C}(\text{s}) \rightleftharpoons \text{CaC}_2(\text{s}) + \text{CO}(\text{g})$ | +1           | Reactants  | Products   |
| $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$             | +0.5         |  |  |
| $\text{CO}_2(\text{g}) + \text{NaOH}(\text{s}) \rightleftharpoons \text{NaHCO}_3(\text{s})$                     | -1           | Products   | Reactants  |
| $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$                 | -1           |  |  |
| $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$                        | -1           |  |  |
| $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$  | 0            | No effect  | No effect  |
| $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$                           | 0            |  |  |

### 6.3.3 Effect of Change of Temperature

Le Chatelier's principle also predicts how a change in the temperature affects an equilibrium system. Heat is a "product" in an exothermic reaction, so if you add heat, the reaction will move to the left to consume the added heat. As a result more reactants form, and product is consumed. Heating an endothermic reaction causes the system to form additional products. Thus, if you change the temperature of a reaction, the value of  $K_{\text{eq}}$  changes.

The influence of temperature can be seen by studying the formation of sulphur trioxide:



The formation of sulphur trioxide is an exothermic reaction; when heated, the system forms additional reactants as a reaction occurs to consume the added heat.

Increasing the temperature of an exothermic reaction decreases  $K_{\text{eq}}$ , so more reactants form.

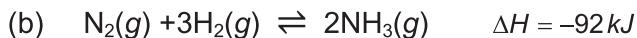
When this reaction is studied at laboratory temperatures, this exothermic reaction proceeds towards the formation of  $\text{SO}_3$ . At high temperatures, such as those found in a furnace, the equilibrium constant becomes much less than 1 and sulphur trioxide decomposes to sulphur dioxide and oxygen.

So you see, that these results match with that of Le Chatelier's principle. The numerical value of  $K_{\text{eq}}$  changes with temperatures, so it is important to specify the temperature when describing a system at equilibrium.

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#### Example 6.7: Influence of temperature changes on equilibrium

How does an increase in temperature influence each of the following equilibria?

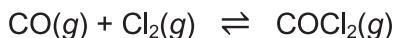


### Solution

- (a) The reaction is endothermic, so, if you increase the temperature, the equilibrium shifts toward products. The equilibrium constant increases as the temperature is increased, so more products form.
- (b) The reaction is exothermic, so if you increase the temperature, the equilibrium shifts toward reactants. The equilibrium constant decreases with increasing temperature, so more reactants form.

### SAQ 4

For the formation of phosgene  $\Delta H$  is  $-108 \text{ kJ}$



In which direction does the system react if temperature is increased?

### 6.3.4 Effect of Addition of Inert Gas

You may come across situations when an inert or a non-reactive gas is added to a reaction container. In most cases they do not react or affect the partial pressures of the reactants or products. So the pressures of materials other than the reactants or products have no effect on the equilibrium due to addition of such material. For example, the  $\text{SO}_3-\text{SO}_2$  equilibrium when studied in the presence or absence of other gases, the results are the same as long as the other gases do not participate in the reaction.

Now let us discuss the effect of addition of inert gas on the equilibrium constant. There are two cases on which equilibrium depends. These are:

- (1) **Addition of an inert gas at constant volume:** When an inert gas is added to the system in equilibrium at constant volume, then the total pressure will increase. But the partial pressures of gaseous reactants and of the products will not change and the equilibrium will not change. Hence, when an inert gas is added to the system in equilibrium at constant volume there will be no effect on the equilibrium.
- (2) **Addition of an inert gas at constant pressure:** When an inert gas is added to the system in equilibrium at constant pressure, then the total volume will increase. Hence, the partial pressure of gaseous products will decrease. Therefore, the equilibrium will shift towards the direction in which there is increase in number of moles of gases. For example: Consider the following reaction in equilibrium:

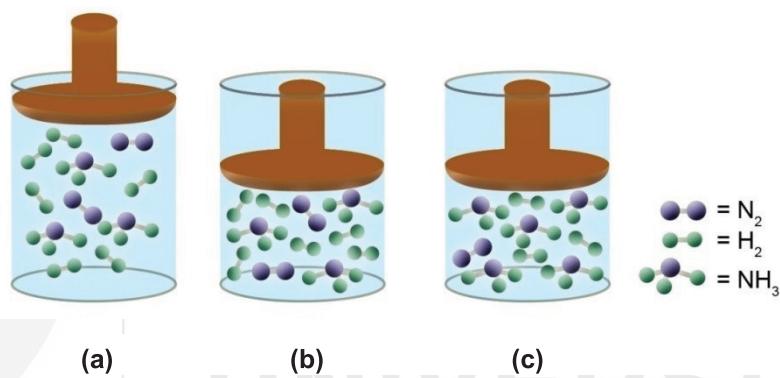


The addition of an inert gas at constant pressure to the above reaction will shift the equilibrium towards the forward direction because the number of moles of gaseous products is more than the number of moles of the gaseous reactants.

### 6.3.5 Effect of Addition of Catalyst

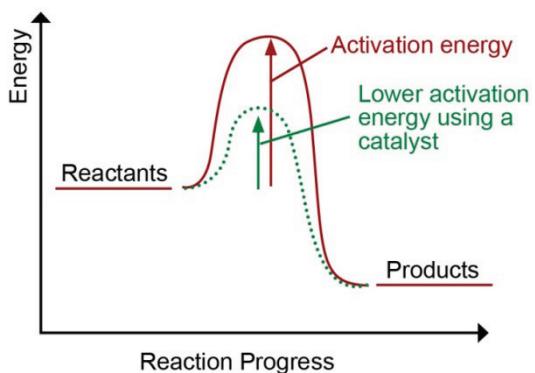
It must be known to you that catalysts only speed up the rate of a reaction, but addition of catalyst makes no difference to the position of equilibrium. Can you say why is it so? It is because a catalyst speeds up the forward and reverse reaction to the same extent. Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium. Then why do the chemists use a catalyst? Well the reason is, for a dynamic equilibrium to be set up, the rates of the forward reaction and the reverse reaction have to become equal. Now, this doesn't happen instantly. For a very slow reaction, it could take years! A catalyst speeds up the rate at which a reaction reaches dynamic equilibrium.

Also remember that catalysts are compounds that accelerate the progress of a reaction without being consumed. Common examples of catalysts include acid catalysts and enzymes. Reactions proceed faster through a lower-energy transition state with the help of catalysts. The energy of the transition state, which is the rate-limiting step, is lowered by catalysts. Thus there is reduction in the necessary energy of activation to allow a reaction to proceed and, in the case of a reversible reaction, reach equilibrium more rapidly.



**Fig. 6.2: Qualitative effect of pressure and volume on the equilibrium**

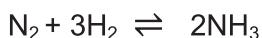
$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ . (a) A mixture of gaseous  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  at equilibrium. (b) When the pressure is increased by decreasing the volume, the mixture is no longer at equilibrium ( $Q_c < K_c$ ). (c) Reaction occurs from left to right, decreasing the total number of gaseous molecules until equilibrium is re-established ( $Q_c = K_c$ ).



**Fig. 6.3: Lowering of the energy of the transition state with catalyst.**

**Example 6.8:**

Given this reaction at equilibrium:



In which direction, toward reactants or toward products, does the reaction shift if the equilibrium is stressed by each change?

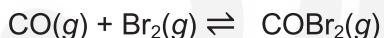
1. H<sub>2</sub> is added.
2. NH<sub>3</sub> is added.
3. NH<sub>3</sub> is removed.

**Solution**

1. If H<sub>2</sub> is added, there is now more reactant, so the reaction will shift toward products to reduce the added H<sub>2</sub>.
2. If NH<sub>3</sub> is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH<sub>3</sub>.
3. If NH<sub>3</sub> is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

**SAQ 5**

Given this reaction at equilibrium:

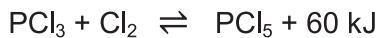


Can you say which direction the reaction will shift if the equilibrium is stressed by the following change?

- i. Br<sub>2</sub> is removed.
- ii. COBr<sub>2</sub> is added.

**SAQ 6**

Predict the effect of increasing the temperature on this equilibrium.



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## 6.4 SUMMARY

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In this unit, we have discussed the applications of equilibrium studies and Le Chatelier's Principle. The effect of change in concentration, pressure, temperature to the chemical equilibrium have also been discussed in detail. Also in this unit, clues have been given as to how to predict the response of an equilibrium system to changes in conditions by applying Le Chatelier's principle. Also discussions have been carried out to understand the effect of addition of inert gas to the chemical equilibrium as well as evaluate the effect of a catalyst on a chemical equilibrium.

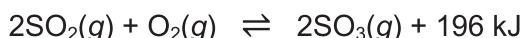
## 6.5 TERMINAL QUESTIONS

- State Le Chatelier's principle.
- Given this equilibrium, predict the direction of shift of equilibrium for each stress.



- a) decreased temperature
- b) increased pressure
- c) removal of HI

- Given this equilibrium, predict the direction of shift of equilibrium for each stress.



- a) removal of SO<sub>3</sub>
- b) addition of O<sub>2</sub>
- c) decreased temperature

- Given this equilibrium, predict the direction of shift of equilibrium for each stress listed.



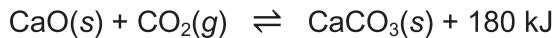
- a) addition of CO
- b) increased pressure
- c) addition of a catalyst

- The synthesis of NH<sub>3</sub> uses this chemical reaction.



Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH<sub>3</sub>.

- The synthesis of CaCO<sub>3</sub> uses this chemical reaction.



Identify three stresses that can be imposed on the equilibrium to maximize the amount of CaCO<sub>3</sub>.

## 6.6 ANSWERS

### Self-Assessment Questions

- The order from most reactant-favoured to least reactant-favoured is (a), (b), (c). First, find out the form of the equilibrium constant expressions of all the reactions. If they have similar ones then the smaller the equilibrium constant is, the less product-favoured (more reactant-favoured) the reaction is. The equilibrium constant expressions are all of the same form because H<sub>2</sub>O(l) does not appear in the expressions for (a) and (b). The equilibrium constants for reactions (a) and (b) are  $1.8 \times 10^{-5}$  and

$1.8 \times 10^{-4}$ , respectively. The equilibrium constant for reaction (c) is not given in Table 6.1, but  $K_c$  for the reverse reaction is given as  $1.7 \times 10^2$ . Because the reaction is reversed, it is necessary to take the reciprocal which gives an equilibrium constant for reaction (c) of  $5.8 \times 10^{-3}$ . Therefore the most reactant-favoured reaction (smallest  $K_c$ ) is (a), the next smallest  $K_c$  is for reaction (b), and the largest  $K_c$  is for reaction (c), which is the least reactant-favoured. So the answer is all reactions are reactant-favoured.

$$2. Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.184 \times 2)^2}{(0.102)^2 (0.0132)} = 986.10$$

Which is much larger than 245, the value of  $K_c$ . Thus the product concentrations are bigger than that at equilibrium. So in order to attain equilibrium, some  $\text{SO}_3$  will form  $\text{SO}_2$ . As the reverse reaction takes place,  $Q_c$  becomes smaller until it becomes equal to  $K_c$ .

3. The system produces additional  $\text{NH}_3$ . The numbers of moles of gas on the reactant and product sides of the chemical equation are to be checked. If there are any liquids or solids then consider their volume negligible compared with that occupied by gases. If a reaction has the same number of moles of gas on both sides, then changes in volume or pressure do not cause any net reaction. We define  $\Delta n_g$  as the change in the number of moles of gases (number of moles of product gases – number of moles of reactant gases) and can arrive at some qualitative conclusions, shown in Table 6.1.
4. The reaction shifts to the left, forming more  $\text{CO}$  and  $\text{Cl}_2$ . If the temperature is increased then the left (reactant) side is favoured, since the reverse reaction is endothermic.
5. i. toward reactants  
ii. toward reactants
6. Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

## Terminal Questions

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.
2. a) towards reactants b) no effect c) towards products
3. a) towards products b) towards products c) towards products
4. a) towards reactants b) towards reactants c) no effect
5. increased pressure, decreased temperature, removal of  $\text{NH}_3$
6. increased pressure, decreased temperature, addition of  $\text{CO}_2$